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POLAROGRAPHIC DETERMINATION OF TRACE AMOUNT OF TITANIUM USING CATALYTIC CURRENT IN THE PRESENCE OF CHLORATE

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Titanium (IV) oxalate complexes are reduced catalytically in the presence of chlorate and this gives rise to an enhancement in sensitivity. Experimental conditions such as acid strength and the concentrations of chlorate, oxalate etc. were standardized to extend the linearity of calibration graph to low titanium concentrations. The interfering effect of other metal ions like Fe(III), Mo(VI), Cu(II), Bi(III), Pb(II), Cd(II), Ni(II), Cr(III), Cr(VI) and Zn(II) on the catalytic current of Ti(IV) was investigated. The detection limit for the determination of Ti(IV) by this method was found to be 5 ng ml^{-1}.

Keywords: Polarography, catalytic current, titanium, chlorate

INTRODUCTION

The catalytic activity of titanate ions in acidic oxalate solution containing an oxidizing agent like chlorate or hydroxylamine is well known [1-4] but it is not widely employed for analytical purposes. The catalytic rate constant is very high when chlorate is used as oxidizing agent (k is of the order of $10^4 s^{-1} M^{-1}$). Hence there is a considerable enhancement in peak current in the presence of chlorate.

Even though the remarkably high sensitivity of catalytic wave is valuable for analytical applications, the experimental conditions must be carefully controlled to obtain a linear relationship between catalytic current and cencentration. Very frequently, for a catalytic process, both linear and nonlinear limiting current vs concentration relationships can be obtained [5]. Thus we found that the experimental conditions used by some earlier workers [6] for the determination of Ti(IV) could not be used at titanium concentrations less than 1 μg ml^{-1} as the calibration graph was not linear below this level. In the present work, experimental conditions such as acid strength, concentrations of complexing agent (oxalic acid) and oxidizing agent (sodium chlorate) were standardized to obtain a linear relationship between catalytic current and titanium concentration in the range of 0.01 - 1.0 μg ml^{-1}.

EXPERIMENTAL

The polarograph used as the cell with the three electrodes were described earlier [7]. The droptime was mechanically controlled. The rate of flow of mercury was 1.862 mg s^{-1}. The capillary characteristic ($m^{2/3}.t^{1/6}$) at t = 2 s was found to be 2.404 $mg^{2/3} s^{-1/2}$. The DPP conditions used were : pulse duration = 0.04 s; pulse height = 50 mV and scan rate = 12 mV s^{-1}. Purified nitrogen was used for deaeration. All measurement were carried out at 298 K.

All reagents used were of analytical grade. A stock titanium (IV) solution (1000 μg ml^{-1}) was prepared by dissolving high pure titanium powder in dilute (1:10) sulphuric acid and making up to volume. Working standards were prepared by diluting the stock solution. Standard solutions of low Ti(IV) concentrations were prepared fresh daily. Standard solutions of Fe(III), Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), Bi(III), Cr(III) and Cr(VI) were prepared either by dissolving their salts in water or by dissolving the pure metal in dilute acid.

Procedure

Pipette an aliquot containing 2 to 20 μg titanium to a polaographic cell, add 12.5 ml 0.8 M oxalic acid, 2 ml 2.5 M sulphuric acid and 1 ml 2 M sodium chlorate and dilute to 20 ml. Deaerate for 5 min and record the polarogram between 0 and 0.40v vs SCE. The titanium concentration in the sample is determined by the standard addition method.

RESULTS AND DISCUSSION

Composition of supporting electrolyte

The effect of variation of the concentration of chlorate, oxalic acid and the acid strength on the DPP peak current was studied. It was found that the peak current increased with increase in

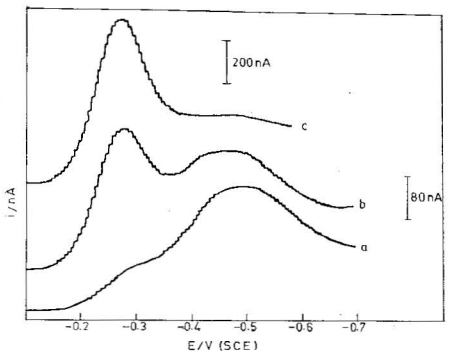

Fig. 1: Differential pulse polarograms of Ti(IV) in a supporting electrolyte containing 0.2 M oxalic acid, 0.25 M sulphuric acid and 0.056 M sodium chlorate. Ti(IV) concentration: (a) 0.1 μg ml^{-1}; (b) 0.4 μg ml^{-1} and (c) 1.04μg ml^{-1}. Experimental conditions: t = 0.5 s; ΔE = 50 mV

chlorate concentration. But excess chlorate was found to yield a broad peak at -0.48 V vs SCE which interfered with the titanium peak at low titanium concentrations. As the titanium (IV) concentration was increased, this second peak due to chlorate decreased in height and finally disappeared at concentrations greater than 1 μg ml^{-1} Ti(IV). This is shown in Fig 1. It was also seen that the interference from the chlorate peak was less when the droptime was increased to 2 s. This is because of the fact that the catalytic current is a function of $t^{2/3}$ whereas the irreversible current due to the reduction of chlorate does not increase much with increase in droptime. The peak current due to the reduction of chlorate at t = 2 s was about 1.2 times the peak current at t = 0.5 s. Hence an optimum chlorate concentration of 0.1 M was employed for further studies. Sodium chlorate was used instead of potassium chlorate because the latter may precipitate out as potassium oxalate in the supporting electrolyte at higher oxalic acid concentrations.

The dependence of peak current on the concentration of oxalic acid was investigated. The peak current increased with the oxalic acid concentration up to 0.2 M and remained constant thereafter. The effect of acid strength on the catalytic current of Ti(IV) was studied in a supporting electrolyte containing 0.4 M oxalic acid and 0.1 M sodium chlorate. The catalytic current increased with increase in sulphuric acid concentration upto 0.5 M and decreased gradually above this level.

Experimental conditions to get a linear calibration graph at low titanium concentrations

In order to extend the linearity of calibration graph to very low titanium concentrations, various compositions of supporting electrolytes were examined. The linerarity was checked by the least square fit of the i_p vs titanium concentration data and this was done by y-residual minimization. The regressional parameters are summerized in Table I. It was seen that the correlation coefficient approached unity as oxalic acid concentration was increased.

Earlier Ferri and Buldini [6] had standardized the concentrations of potassium chlorate, oxalic acid and sulphuric acid to get best results and found these concentrations to be 0.1 M, 0.2 M and 0.25 M respectively. But we found that the calibration graph was nonlinear below 1 μg ml^{-1} under these conditions. Our results showed that in a supporting electrolyte containing 0.5 M oxalic acid, 0.11 M sodium chlorate and 0.25 M sulphuric acid, the catalytic current was proportional to titanium concentrations to a lavel of 0.01 μg ml^{-1} (at t = 2 s). A higher droptime was found to be preferrable both from the point of view of sensitivity and linearity.

TABLE I: Summary of regressional parameters for calibration graph of titanium under various experimental conditions

Supporting electrolyte	cocentration range (ppm)	slope (μA/ppm)	intercept (μA)	correlation coefficient	No. of data points
0.16M oxalic acid +0.2M sulphuric acid +0.13M chlorate	0.77-2.73	2.324	0.842	0.9887	5
0.2M oxalic acid +0.25M sulphuric acid +0.11M chlorate	0.77-2.61	2.852	–0.0657	0.9938	6
0.4M oxalic acid +0.25M sulphuric acid +0.11M chlorate	0.20- 1.3	2.070	0.0534	0.9994	5
0.5 oxalic acid + 0.2M sulphuric acid +0.11M chlorate	0.01-0.283	2.028	–0.0033	0.9998	6

Comparison of differential pulse polarography (DPP) and charging current compensated polarography (CCCDCP) for the determination of Ti(IV)

A comparison of the sensitivities of the catalytic current of Ti(IV) by DPP and CCCDCP was done and it was found that the decatalytic current was 2.8 times more sensitive than the DPP catalytic current for a droptime of 0.5 s. This value agreed well with the theoretical ratio of i(CCCDCP) to i(DPP) calculated with the expression derived by Rodriguez-Monge et al [8]. Earlier, we had obtained similar results [9] for the catalytic current of Mo(VI) in the presence of nitrate. Even though CCCDCP was more sensitive than DPP, the latter gave better resolution. Hence DPP was preferrable at very low titanium concentrations where it was necessary to reslove the peak due to titanium catalytic current from the broad peak due to the irreversible reduction of excess of chlorate. DPP also has an advantage for the determination of titanium in the presence of copper and bismuth because of its higher resolution compared to CCCDCP.

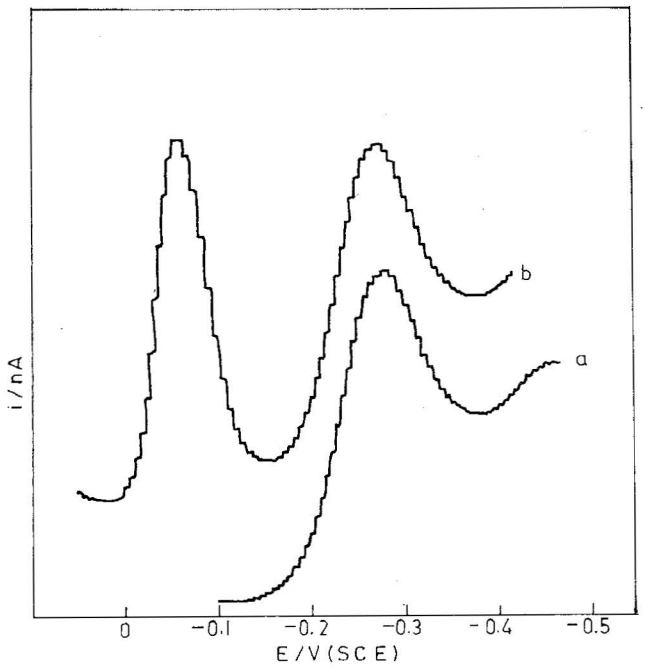

Fig. 2: Influence of Cu(II) on the catalytic peak current of Ti(IV). Supporting electrolyte and DPP conditions same as in Fig 1 (a) [Ti(IV)] = 0.4μg ml^{-1}; (b)[Ti(IV)] = 0.4 μg ml^{-1} and [Cu(II)] = 5.0 μgml^{-1}

Influence of diverse ions

Cations like Al(III), Pb(II), Cd(II), Ni(II), and Zn(II) did not interfere when present in about 100-fold weight ratio to titanium. 10-fold amount of Mo(VI) and Cr(III) also did not interfere. There was no interference from equal quantities of copper (II) and bismuth(III) but larger amounts interfered since the reduction of both Cu(II) and Bi(III) occured at more positive potentials than that of titanium. The influence of excess of copper on the catalytic current of Ti(IV) is shown in Fig 2. Iron(III) interfered with the catalytic current of titanium. Up to 25-fold amount of ferric iron had no effect on the catalytic current of titanium but it increased if the Fe(III) concentration was increased above this level. Thus the presence of 100-fold amount of iron(III) resulted in a 28% increase in the catalytic current. Chromium(VI) interfered seriously with the catalytic current of Ti(IV). Thus at a chromium(VI) to titanium(IV) weight ratio of 2.5, the DPP catalytic current was increased by 23%.

TABLE II : Result for the estimation of titanium in synthetic solutions

Ti added (μg)	Ti found (μg)	Error (%)
4.0	3.80	-5.0
10.0	9.80	-2.0
20.0	19.58	-2.1
50.0	49.10	-1.8

Determination of Ti(IV) in synthetic solutions

Synthetic solutions of water samples were prepared by adding known amount of titanium(IV) to 100 ml distilled water and these were analyzed using catalytic current polarography. The results are given in Table II. The accuracy was very good except at very low Ti(IV) concentrations. Thus at titanium concentrations of 0.10 μg ml^{-1} and above, the error was about 2% whereas at 0.4 μg ml^{-1} Ti(IV) level, the error was 5%. The relative standard deviation for 5 replicate measurements at 0.10 μg ml^{-1} Ti(IV) was found to be 3%. The detection limit for titanium by this method was found to be 5 μg ml^{-1}.

REFERENCES

1. J Koryta and J Tenygl, *Collect Czech Chem Commun*, **19** (1954) 839
2. A Blazek and J Koryta, *Collect Czech Chem Commun*, **18** (1953) 326
3. K Nakano, K Tanaka and H Muroi, *Bunseki Kagaku*, **19** (1970) 1680
4. N K Ignatova, P M Zaitsev and M Yu Gornostaeva, *Zh Anal Khim*, **33** (1978) 2140
5. A M Bond, *"Modern Polarographic Methods in Analytical Chemistry"*, Marcel Dekker Inc, New York, (1980) p 109
6. D Ferri and P L Buldini, *Analyst*, **107** (1982) 1375
7. Bharathibai J Basu and S R Rajagopalan, *Indian J Technol*, **27** (1989) 232
8. L M Rodriguez-Monge, E Munez, J L Avila and L Camacho, *Anal Chem*, **60** (1988) 2269
9. Bharathibai J Basu, D K Padma and S R Rajagopalan, *Talanta*, **38** (1991) 1431